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(54) Title: SILVER TERNARY ALLOY

(57) Abstract: A firestain and tarnish-resistant ternary alloy of silver, copper and germanium contains from more than 93.5 wt% to 95.5 wt% Ag, from 0.5 to 3 wt% Ge and the remainder, apart from incidental ingredients (if any), impurities and grain refiner, copper. In order to further protect an article made from the alloy, it may be surface treated with an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide.

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SILVER TERNARY ALLOY

FIELD OF THE INVENTION

5 The present invention relates to a ternary alloy of silver, copper and germanium, to finished or semi-finished shaped articles made from the alloy, and to the use for the surface treatment of the alloy with alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide.

10 BACKGROUND TO THE INVENTION

 Since ancient times it has been appreciated that unalloyed 'fine' silver is too soft to withstand normal usage, and it has been the practice to add a proportion of a base metal to increase hardness and strength. In the UK, legislation that has existed since the fourteenth century specifies a minimum
15 silver content of articles for sale at 92.5% (the Sterling standard) or 96% (the Britannia standard), but does not specify the base metal constituents. Experience convinced early silversmiths that copper was the most suitable of the metals available to them. Modern silver-sheet manufacturers generally adhere to this
20 composition, although sometimes a proportion of copper is replaced by cadmium to attain even greater ductility. Sterling with a 2.5% cadmium content is permitted to be used in the UK for spinning and stamping, although the use of cadmium is becoming less widespread because when the alloy is in the molten state fumes of cadmium are given off and are toxic. For that reason, a specific
25 alloy composition is produced in continental Europe that contains 93.5 wt% silver. It is sold as a sterling grade alloy with enhanced forming properties for deep drawing or spinning operations. The high silver content reduces the hardness of the alloy, but not to a level where a finished item would be too soft and subject to excessive damage from handling. It therefore can provide a
30 cadmium-free spinning grade, sold to perform similar forming operations to the cadmium-containing silver grades available in the UK.

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The relatively high value assigned to silver compared to the other alloying constituents in the different grades has meant that manufacturers have aimed to produce their alloys as closely as possible to the minimum legal silver content. This has also resulted in a system in the UK of ensuring that the minimum silver content is assured by means of independent external verification – the Assay Office System.

In all but the largest manufacturing companies, most of the annealing and soldering required to assemble finished or semi-finished articles is carried out with the flame of an air-gas blowtorch. The oxidising or reducing nature of the flame and the temperature of the articles are controlled only by the skill of the silversmith. Pure silver allows oxygen to pass easily through it, particularly when the silver is heated to above red heat. Silver does not oxidise in air, but the copper in a silver/copper alloy is oxidised to cuprous or cupric oxide. Pickling of the oxidised surface of the article in hot dilute sulphuric acid removes the superficial but not the deeper seated copper oxide so that the surface consists of fine or unalloyed silver covering a layer of silver/copper oxide mixture. The pure silver is easily permeated during further heating, allowing copper located deeper below the surface to become oxidised. Successive annealing, cold working and pickling produces a surface that exhibits the pure lustre of silver when lightly polished but with heavier polishing reveals dark and disfiguring stains known as 'fire-stain' or 'fire'. Soldering operations are much more productive of deep fire-stain because of the higher temperatures involved. When the depth of the fire-stain exceeds about 0.025mm (0.010 inches) the alloy is additionally prone to cracking and difficult to solder because an oxide surface is not wetted by solder so that a proper metallurgical bond is not formed.

Secondly, it is a well-known fact that with exposure to everyday atmospheric conditions, silver and silver alloys develop a lustre-destroying dark film known as tarnish.

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The addition of germanium to silver alloys was found to offer a solution to both these problems. Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) disclosed a novel silver alloy that maintained the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys were ternary Ag-Cu-Ge alloys containing at least 92.5 wt% Ag, 0.5-3 wt% Ge and the balance, apart from impurities, copper. The alloys were stated to be stainless in ambient air during conventional production, transformation and finishing operations, to be easily deformable when cold, to be easily brazed and not to give rise to significant shrinkage on casting. They were also stated to exhibit superior ductility and tensile strength and to be annealable to a required hardness. Germanium was stated to exert a protective function that was responsible for the advantageous combination of properties exhibited by the new alloys, and was in solid solution in both the silver and the copper phases. The microstructure of the alloy was said to be constituted by two phases, a solid solution of germanium and copper in silver surrounded by a filamentous solid solution of germanium and silver and copper. The germanium in the copper-rich phase was said to inhibit surface oxidation of that phase by forming a thin GeO or GeO₂ protective coating which prevented the appearance of fire-stain during brazing and flame annealing which results from the oxidation of copper at high temperatures. Furthermore the development of tarnish was appreciably delayed by the addition of germanium, the surface turned slightly yellow rather than black and tarnish products were easily removed by ordinary tap water. The alloy was said to be useful *inter alia* in jewellery. However, the alloy disclosed in the above patent suffers limitations insofar as it can exhibit large grain size, leading to poor deformation properties and formation of large pools from low-melting eutectics resulting in localised surface melting when the alloy is subject to the heat of an air torch.

Furthermore, patents US-A-6168071 and EP-B-0729398 (Johns) disclosed a silver/germanium alloy which comprised a silver content of at least 77 wt % and

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a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contained elemental boron as a grain refiner at a concentration of greater than 0 ppm and less than 20ppm. The boron content of the alloy could be achieved by providing the boron in a master copper/boron alloy having 2 wt % elemental boron. It was reported that such low concentrations of boron surprisingly provided excellent grain refining in a silver/germanium alloy, imparting greater strength and ductility to the alloy compared with a silver/germanium alloy without boron. The boron in the alloy inhibited grain growth even at temperatures used in the jewellery trade for soldering, and samples of the alloy were reported to have resisted pitting even upon heating repeatedly to temperatures where in the previously suggested alloys a briefly mentioned copper/germanium eutectic in the alloy would melt. Strong and aesthetically pleasing joints between separate elements of the alloy could be obtained without using a filler material between the free surfaces of the two elements and a butt or lap joint could be formed by a diffusion process or resistance or laser welding techniques. Compared to a weld in Sterling silver, a weld in the above-described alloy had a much smaller average grain size that improved the formability and ductility of the welds, and an 830 alloy had been welded by laser welding and polished without the need for grinding. It may be noted with regard to the above mentioned eutectic that although its adverse effects are reduced by the reduction in grain size, the ability of the eutectic to form and become molten on post-formation thermal treatment is retained because that is governed by the chemical composition of the alloy rather than its crystal structure.

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Silver alloy according to the teaching of GB-B-2255348 and EP-B-0729398 is now commercially available in Europe and in the USA under the trade name Argentium, and the word "Argentium" as used herein refers to these alloys. The 925 grade Argentium alloy comprises 92.5 wt% (minimum) Ag, 1.1-1.3 wt% Ge, 6 ppm B, the balance being copper and impurities. The alloy shows excellent resistance to tarnishing even under very arduous conditions. A passive layer is

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formed by the germanium, which significantly slows the formation of silver sulphide, the main cause of tarnishing on conventional silver alloys. Even in a hydrogen sulphide atmosphere the degree and depth of tarnish is significantly less compared to a conventional silver alloy or a silver plated item. The same
5 mechanism that creates the tarnish resistance also results in the formation of a passive layer which significantly reduces the depth of 'fire-staining' or the 'fire layer' that is produced in this alloy when torch annealing in air. Trials have shown that the depth of the 'fire-staining' to be up to three times greater in conventional silver alloys compared to the Argentium silver alloys. This reduces
10 the amount of polishing that the alloy requires and can result in other considerable cost savings in manufacturing.

Despite the advantages of existing Argentium alloy grades, there is a need for further improvement of the alloy with respect to its stability under thermal
15 processing and in particular to its resistance to pitting and/or sagging when heated for the purposes of annealing or joining. There is also a need for alloys that combine these favourable properties with hardness and resistance to tarnishing. There is a further need for alloys that on investment casting has a reduced propensity to formation of "hot short" (cracking) defects.

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As a further matter, so far as long-term tarnish resistance is concerned, various proposals have been made for cleaning or protecting Sterling silver and other known grades of silver to remove tarnish and/or to inhibit the formation of tarnish. GB-A-1130540 is concerned with the protection of a finished surface of
25 Sterling or Britannia silver as a step in a production run, and discloses a process that comprises the steps of:

wetting a clean silver surface of an article with a solution comprising 99 parts by weight of a volatile organic solvent, for example trichloroethylene or 1,1,1-trichloroethane and from 0.1-1.8 parts by weight of an organic solute
30 containing a -SH group and capable of forming a transparent colourless

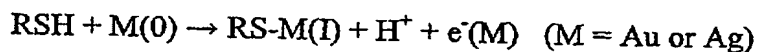
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protective layer on the silver surface, for example stearyl and cetyl mercaptan or thioglycollate;

allowing the solution to react with the surface to form such a layer and allowing the solvent to evaporate; and

5 washing the surface with a detergent solution, rinsing the surface with hot water and allowing it to dry. The above process is stated to provide a "long-term finish" intended to last the intended shelf-life until the article reaches the user.

Treatments of the above kind are believed to result in the formation of a
10 self-assembled coating derived from the thiol compounds in which the sulphur atoms are bound onto the metal surface and the alkyl tails are directed away from the metal surface, see US-A-6183815 (Enick). Yousong Kim *et al*, <http://www.electrochem.org/meetings/past/200/abstracts/symposia/h1/1026.pdf> reported that the adsorption of thiols onto silver proceeds through an anodic
15 oxidation reaction that produces a shift of the open circuit potential of the substrate metal in the negative direction or if the potential is fixed an anodic current peak:



Kwan Kim, *Adsorption and Reaction of Thiols and Sulfides on Noble Metals*,
20 Raman SRS-2000, 14-17 August 2000, Xaimen, Fujian, China, <http://pcoss.org/icorsxm/paper/kuankim.pdf>, also discloses the formation of self-assembled monolayers and discloses that alkanethiols, dialkyl sulfides and dialkyl disulfides self-assemble on silver surfaces with aliphatic dithiols forming dithiolates by forming two Ag-S bonds. In contrast, the literature on formation
25 of alkylthiols of germanium is relatively sparse. The reaction of alkanethiols with Ge to form a high quality monolayer has been reported in the context of semiconductor and nanotechnology by Han *et al*, *J. Am. Chem. Soc.*, **123**, 2422 (2001). In the experiment described, a Ge(111) wafer is sonicated in acetone to dissolve organic contaminants and immersed in concentrated HF to remove
30 residual oxide and produce a hydrogen-terminated surface, after which the wafer

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is immersed in an alknaethiol solution in isopropanol, sonicated in propanol and dried.

SUMMARY OF THE INVENTION

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Although GB-B-2255348 discloses a range of silver content from Sterling to Britannia grades, as previously explained a skilled person would not contemplate using a silver content above the legal minimum for the intended grade because of the cost of the silver. He is not given by the disclosure of that patent or that of the subsequent patents relating to the ternary alloys any incentive to adopt intermediate silver contents. However, it has now been found that silver-copper-germanium ternary alloys having silver contents between those of the Sterling and Britannia grades possess valuable properties that facilitate both casting, welding and other thermal treatments used in the manufacture of silver articles.

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In particular, the applicants have become aware of the desirability of reducing or avoiding the formation and/or melting of the above mentioned binary copper-germanium eutectic which melts at 554°C. During the production of e.g. 925 Argentium silver alloys, the formation of this phase can be avoided by careful control of the casting conditions since under equilibrium cooling conditions the crystallisation is complete at below 640°C. However, this binary phase can create problems during subsequent thermal treatment of the alloys, e.g. using brazing alloys which typically have melting points in the range 680-750° and torch annealing which typically involves heating a workpiece to a dull red heat at 700-750°C. On heating the workpiece to or beyond these temperatures incipient melting occurs with a small amount of material corresponding to this binary phase becoming molten while the bulk remains stable. When the workpiece returns to ambient temperature, porosity develops where the alloy has liquefied. This contributes brittleness and e.g. as noted in GB-B-2255348 there is a tendency for the alloy to sag when heated for joining or annealing operations. Although the use

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of the boron grain refiner of US-A-6168071 and EP-B-0729398 significantly reduces the pitting and sagging consequent on formation and melting of the binary eutectic, the formation and melting of that eutectic is, as previously mentioned, not eliminated and there is still scope for the further development of the ternary alloy to improve its pitting and sagging properties. By increasing the silver content above the level for Sterling but less than that for Britannia it is possible to produce an alloy in which the above binary eutectic either does not form or gives rise to reduced problems in subsequent heat treatment. This provides alloys with a much greater inherent stability under thermal processing.

The germanium addition prevents the reduction in hardness that would be seen in a silver-copper alloy of this composition. The alloy also shows resistance to tarnishing, even under very arduous test conditions.

The invention therefore provides a ternary alloy of silver, copper and germanium containing from more than 93.5 wt% to 95.5 wt% Ag, from 0.5 to 3 wt% Ge and the remainder, apart from incidental ingredients, impurities and grain refiner, copper.

A typical alloy that has been found to be suitable contains about 94.5 wt% Ag, about 4.3 wt% Cu and about 1.2 wt% Ge. In the above alloy the weight ratio of Cu to Ge is about 3.6:1 whereas in the existing 925 grade Argentium the ratio can be from 5.8:1 (1.1 wt% Ge) to 4.8:1 (1.3 wt% Ge). The applicants consider that it is the reduction in the Cu:Ge weight ratio that is responsible for the reduced thermal processing problems, the CuGe eutectic either not forming or forming in a significantly reduced amount during post-melt thermal processing. In particular the ratio is preferably from 4:1 to 3:1, more preferably about 3.5:1. Above 4:1 the alloy is more likely to exhibit firestain, whereas below 3:1 the high germanium content gives rise to formability problems.

In the above alloy, preferred Ag contents range from about 94.0 to about 95.5 wt%, lower values being preferred for reducing the expense of the silver

used. It has been found, surprisingly, that if the Ag content is increased to 96 wt% it is difficult to avoid firestain even at high Ge contents. As regards Ge, contents of from 1.0 to 2.0 wt% are preferred. Below 1.0 wt% Ge, consistent resistance to firestain and tarnish may not be obtained, whereas above 2 wt% Ge there is an increasing risk of embrittlement of the alloy. Furthermore, Ge is expensive and its expense makes it desirable to reduce its content to a minimum. The applicants have found that consistent resistance to firestain and tarnish are obtained at Ge contents of from 1.1 to 1.3 wt%. The alloy will preferably further comprise boron in an amount effective for grain refinement, typically 1-40 ppm and preferably 5-10 ppm. Excessive amounts of boron may give rise to boron hard spots, but in the case of alloys supplied for casting it will often be desirable to incorporate relatively large amounts of boron to compensate for losses on re-melting.

The alloy may contain one or more incidental ingredients known per se in the production of silver alloys in amounts that are not detrimental to the mechanical strength, tarnish resistance and other properties of the material. For example, zinc may be added e.g. in an amount of about 0.5 wt% to reduce the melting point of the alloy, to add whiteness, to act as a copper substitute, as a deoxidant and to improve the fluidity of the alloy. Cadmium may also be added in similar amounts although its use is presently not preferred. Tin may be added, typically in an amount of 0.5 wt%. Indium may be added in small quantities e.g. as a grain refiner and to improve the wettability of the alloy. Silicon may also be added in e.g. amounts of 0.1 to 1 wt%.

The alloy may be produced by continuous casting. The initial casting conditions may be as for an equivalent silver-copper grade except that the germanium addition will give solidus and liquidus temperatures approximately 15°C lower than the equivalent silver-copper alloys. The germanium content also alters the emissivity of the alloy. This will affect the rate at which heat can be removed from the die (if continuous casting) or standing time (if static casting). It may also be desirable to re-calibrate optical (infra-red) pyrometers when casting

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the present tertiary alloys. This is because the germanium content gives the alloys a different emissivity. Typically the sensors would give a much lower reading than the actual temperature if they were not adjusted. During billet production from continuously cast slabs it is a requirement to remove the surface layer, which has been in contact with the die. This is the layer that acted as the starting point for solidification of the metal and it contains the most impurities. To remove this layer a minimum of 0.01 mm should be removed from each side of the cast slab by either a mechanical or an abrasive technique.

To produce a sheet with an internal structure suitable for further use by the silversmith a rolling regime which contains a minimum of two 50% reductions and two anneals is recommended. This will remove the 'as-cast' grain structure and prevent any orange peel effects when the sheet is being formed by the silversmith. As an example, to produce sheet at 2.5 mm thick the following would be the minimum rolling requirements:

	Starting size	10 mm thick	
	Roll to	5.0 mm thick	(50% reduction)
	Anneal		
20	Roll to	2.5 mm thick	(50% reduction)
	Anneal		

When cross-rolling to increase the width of sheets, at the end of the cross-rolling regime the sheet should be annealed prior to the commencement of the normal rolling schedule.

When drawing the alloy into wire, the required drawing sequence depends on the internal grain structure of the starting material. This is because the wire could be from two possible sources, either a cold or warm working operation (e.g. extrusion) or from an 'as-cast' wire size (e.g. a 'mini' casting system). For material that has come from a previous cold worked source the only constraint is

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that the material has a minimum of 25% cold work prior to each anneal. This will prevent excessive grain growth. A maximum of 60% cold work between each anneal is recommended. For example, the following work procedures would apply to wire from a previously cold worked source:

5	Starting size	6 mm diameter	
	Draw to	5.2 mm diameter	(25% reduction)
	Or		
	Starting size	6 mm diameter	
	Draw to	3.8 mm diameter	(60% reduction)
10	Anneal		
	Draw to	2.4 mm diameter	(60% reduction)
	Anneal	etc.	

For material that is from a cast source then a drawing sequence involving two reductions of a minimum of 50% and two anneals recommended to give a grain size suitable for further work by the silversmith. Work procedures would be similar to those given above.

When annealing the alloy, it is important that the furnace gas, although protective, does not deplete the surface layer of germanium, as this will reduce the tarnish resistance of the alloy and its resistance to "fire stain". It is the ability of the surface layer of germanium to form a germanium oxide which then acts as a barrier preventing any further penetration of the oxide layer or build up of tarnishing products. For this reason a furnace atmosphere based on cracked ammonia is not recommended. To prevent depletion of the germanium from the surface of the alloy the presence of a small amount of oxygen or a slightly "wet" furnace atmosphere is beneficial. Typically the furnace atmosphere should contain approximately 0.1-0.5% oxygen and have a dew point of 20-40°C. The exact balance of these values depends on the type of furnace being used. It is important that the balance is not set to far in the opposite direction as this may result in oxidation of the copper content of the alloy. The annealing temperature

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may be within the range 620 – 650°C and should preferably not exceed a maximum temperature of 650°C. The annealing time for this temperature range is 30 to 45 minutes.

5 As regards cleaning procedures, although GB-A-1130540 was alleged to provide a long-term finish, in the inventor's experience this type of treatment does not fully solve the difficulties created by tarnish in the period between manufacture and supply to the ultimate purchaser or user and suffers from a number of shortcomings. Although a silver product might arrive at the retailer in
10 an untarnished state, it was largely the result of the wrapping applied by the manufacturer, which protected the article from air. Once the wrapping was removed and the article was displayed in a retail environment such as a display case in a hotel where it was subject to ambient air and the heat of artificial lighting, an article of conventional Sterling silver would require re-polishing after
15 one week and after two weeks would normally be so tarnished as to be unsaleable. At an exhibition, the life of an article on display before significant tarnish sets in may be as short as 3-4 days. Re-polishing produces wear and fine handling scratches, so that unless the article can be sold quickly it loses its pristine appearance. The need to polish display silver at frequent intervals adds to
20 the labour cost of a jeweller or other retail establishment, whose management take the view that its staff should be employed to sell products and not to clean stock. Tarnish at point of sale is therefore a serious problem that reduces the willingness of those in the distribution chain to stock and display silver products, and which has not yet been adequately solved.

25 When the product reaches the ultimate purchaser, it is of course desirable that the task of tarnish removal should be made as infrequent and undemanding as possible.

30 It has now been found that an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide can be used for the surface treatment of the above

described alloys, preferably so as to reduce or further reduce tarnishing of the alloy such that a sample can be subjected to hydrogen sulphide gas above a 20% solution of ammonium polysulphide for at least 30 minutes and typically 45-60 minutes while retaining a generally untarnished appearance.

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The invention also therefore includes the use of an organic compound containing -SH or -S-S- bonds e.g a C₁₂-C₂₄ alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide in the preparation of a tarnish inhibitor for an article of a the silver-copper-germanium alloy described above.

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The invention further provides an alloy of silver as described above, or a shaped article formed of said alloy, that has been treated with a C₁₂-C₂₄ alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide.

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In an accelerated tarnish test in which the article is subject to hydrogen sulphide gas from the ammonium polysulphide solution above which it is suspended at a height of e.g. 30mm corresponds to a period of a year or more in a retail environment where an article is on display and exposed to ambient atmosphere and may be subject to elevated temperatures. It is the combination of the protective function of the germanium content of the alloy with the further protection from the organo-sulphur compound that is believed to be responsible for the observed increase in tarnish resistance. The period during which the article retains its untarnished appearance under these severe conditions may be three or more times the corresponding period for an article that has not been treated with an organo-sulphur compound, which is unexpected because the same accelerated tarnish test carried out under the same conditions on a conventional Sterling silver article not containing protective germanium does not reveal a significant increase in untarnished lifetime between its untreated and organo-sulfur treated states.

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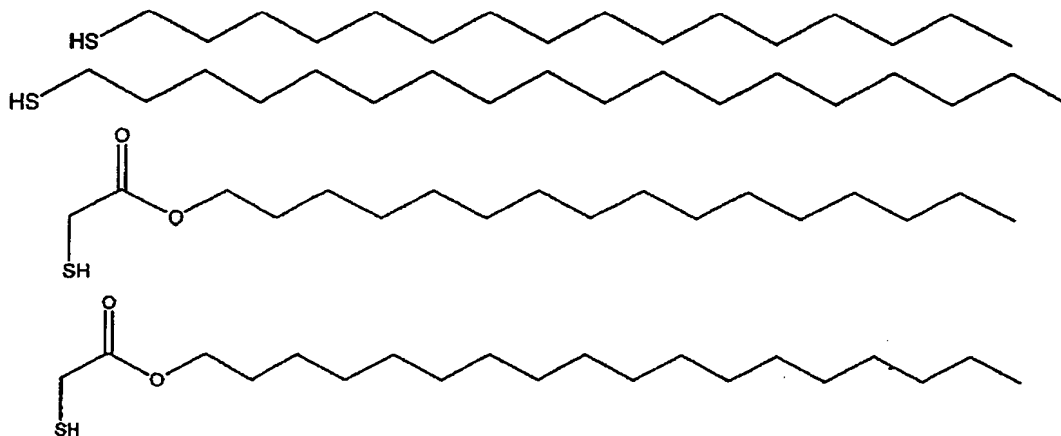
Accelerated tarnishing tests with Argentium Sterling using ammonium polysulphide have been reported by the Society of American Silversmiths, see

<http://www.silversmithing.com/largentium4.htm>

and in a comparative test the Argentium Sterling remained untarnished after one hour whereas conventional Sterling became tarnished after less than 15 minutes. However, in this test 0.5ml of 20% ammonium polysulfide solution is mixed with
 5 200ml of distilled water, so that the test is greatly less severe than when samples are exposed to the 20% solution itself. In WO 02/095082, samples were suspended above 20% ammonium polysulphide, but the exposure times were relatively short, and onset of yellowing was reported for Ag-Cu-Ge alloys after 3-5 minutes exposure. Other tests reported in that specification involve placing
 10 samples in a desiccator containing flowers of sulphur and calcium nitrate and are less severe than the ammonium polysulphide test.

As protective agent there may be used a compound containing a long chain alkyl group and a -SH or -S-S- group, e.g. an alkanethiol, dialkyl sulfide or
 15 dialkyl disulfides in which the chain is preferably at least 10 carbon atoms long and may be C₁₂-C₂₄. The -SH or -S-S- compounds that may be used include straight chain saturated aliphatic compounds containing 16-24 carbon atoms in the chain, for example stearyl mercaptan, cetyl mercaptan (octadecyl mercaptan) and stearyl and cetyl thioglycollates whose formulae appear below.

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Stearyl mercaptan is a white to pale yellow waxy solid that is insoluble in water. The protective agent may be used in solution in a solvent e.g. a non-polar organic solvent such as an alcohol e.g. methyl or ethyl alcohol, a ketone e.g. acetone or methyl ethyl ketone, an ether e.g. diethyl ether, an ester e.g. n-butyl acetate, a hydrocarbon, a halocarbon e.g. methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene or HCFC 141b. The protective agent may comprise 0.1-1 wt% of the solvent. Solvents based on *n*-propyl bromide are presently preferred on the ground of the short atmospheric life of that compound, its relatively low toxicity compared to other halocarbons, its favourable chemical and physical properties and its boiling point, specific heat and latent heat of vaporization.

US-A-5616549 discloses a solvent mixture comprising: 90 percent to about 96.5 percent *n*-propyl bromide; 0 percent to about 6.5 percent of a mixture of terpenes, the terpene mixture comprising 35 percent to about 50 percent *cis*-pinane and 35 percent to about 50 percent *trans*-pinane; and 3.5 percent to about 5 percent of a mixture of low boiling solvents, the low boiling solvent mixture comprising 0.5 percent to 1 percent nitromethane, 0.5 percent to 1 percent 1,2-butylene oxide and 2.5 percent to 3 percent 1,3-dioxolane. The solvent mixture has the following advantages:

- (i) it is properly stabilized against any free acid that might result from oxidation of the mixture in the presence of air, from hydrolysis of the mixture in the presence of water, and from pyrolysis of the mixture under the influence of high temperatures;
 - (ii) it is non-flammable and non-corrosive;
 - (iii) the various components of the solvent mixture are not regulated by the U.S. Clean Air Act; and
 - (iv) none of the various components of the solvent mixture are known cancer causing agents (i.e., the various components are not listed by N.T.L., I.A.R.C. and California Proposition 65, nor are they regulated by OSHA).
- Moreover, the solvent mixture has a high solvency with a kauri-butanol value

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above 120 and, more preferably, above 125. In addition, the solvent mixture has an evaporation rate of at least 0.96 where 1,1,1-Trichloroethane=1. Upon evaporation, the solvent mixture leaves a non-volatile residue (NVR) of less than 2.5 mg and, more preferably, no residue. Solvents made in accordance with the
5 above patent are available from Enviro-Tech International, Inc of Melrose Park, Illinois, USA under the trade name EnSolv.

The surface treatment may be carried out after the manufacturing stages for a shaped article made of the alloy have been completed. The article may be of
10 flatware, hollowware or jewellery. Fabrication steps may include spinning, pressing, forging, casting, chasing, hammering from sheet, planishing, joining by soldering brazing or welding, annealing and polishing using buffs/mops and aluminium oxide or rouge. An article to be treated may be de-greased ultrasonically in a treatment bath, dipped into a bath containing the treatment
15 agent e.g. 1 wt% stearyl mercaptan in solvent e.g. EnSolv, rinsed in one or more baths of the solvent and allowed to dry by evaporation. The solvent should leave no or substantially no residue, so that subsequent washing with water or aqueous solvents should be unnecessary and the article can be allowed to dry. The article may then be packed for delivery into the distribution chain. This may include
20 wrapping the article in one or more protective sheets, placing it in a presentation box, and wrapping the presentation box in a protective wrapping e.g. of heat-shrunk plastics film. Articles which have been treated with an organic compound containing -SH or -S-S- groups as aforesaid and packaged should not only reach their point of sale in good condition but should if displayed e.g. on a shelf or in a
25 cabinet for an extended period, expected to be at least 6 months and possibly 12 months or more, remain without development of significant tarnish.

For many purposes, e.g. light industrial applications, it may be preferred to carry out the anti-tarnish treatment using a predominantly aqueous solvent
30 system. For this purpose, the protective agent may be dissolved in a water-immiscible organic solvent, for example a solvent based on *n*-propyl bromide, the

resulting solution may be mixed with a relatively concentrated water-based soap or detergent composition which acts as a "carrier", after which water is added to the resulting mixture to provide an aqueous treatment dip or combined degreasing and treatment solution. Thus an aqueous dip has the advantages that a solvent
5 degreasing system is not necessary, the dip is easily made and may be used cold, all areas of immersed articles can come into contact with the stearyl mercaptan or other treatment agent, the present alloy only requires 2 minutes in the dip, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished alloy, and the dip can be easily used in a manufacturing
10 environment before articles are sent to retailers.

Preferred water-based detergents may be based on anionic, alkoxylated non-ionic or water-soluble cationic surface active agents or mixtures of them and preferably have a pH at or close to 7. Anionic surfactants may be based on alkyl
15 sulphates and alkyl benzene sulphonates, whose harshness on prolonged skin exposure may be reduced by the co-presence or use of alkyl ethoxy sulphates (US-A-3793233, Rose *et al.*; 4024078 Gilbert; 4316824 Pancherni). Other known surfactants e.g. betaines may also be present, see e.g. US-A-4555360 (Bissett). A suitable formulation containing 5-15 wt% non-ionic surfactants and 15-30 wt%
20 anionic surfactants is available commercially in the UK under the trade name Fairy Liquid (Proctor & Gamble).

An aqueous liquid may also be made by dissolving the treatment agent in a non-organic solvent and adding a relatively concentrated aqueous detergent
25 liquid, for example undiluted Fairy Liquid. This provides a detergent liquid that has a number of advantages: the soapy liquid is easily made, the liquid is easily applied to the articles of the present alloy with a damp sponge/cotton wool/cloth etc, the liquid and lather enables the stearyl mercaptan or other treatment agent to get into those awkward areas on an article where a cloth may not be able to reach,
30 rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, the process can be easily used in a

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manufacturing environment before articles are sent to retailers and can also be easily used in a retail or domestic environment.

The articles may alternatively simply be polished with a polish containing
5 1-5wt% of the organo-sulphur compound e.g. stearyl mercaptan together
surfactants and a cleaning agent e.g. diatomaceous earth in a solvent. As a further
alternative, they may be simply polished with a cloth impregnated with the
organosulphur compound e.g. stearyl mercaptan. The advantages of a cleaning
cloth are that it is easily manufactured, can be easily used in a retail or domestic
10 environment and is good for general upkeep of articles of the present alloy (if
required).

The invention will now be further described, by way of illustration only,
with reference to the following examples. Throughout the examples, the term
15 "enhanced tarnish resistance" of samples treated with stearyl mercaptan refers to
the comparison with samples of Argentium Silver which have not had any
treatment except for polishing and cleaning in EnSolv 765.

Example 1

20 (Production and properties of continuously cast alloy)

A ternary silver-copper-germanium alloy (Ag = 94.5 wt%, Ge = 1.2 wt%,
Cu = 4.1 wt%, B = 0.0008 wt% (8 ppm) is prepared by melting silver, copper and
germanium together at 1050°C under an atmosphere of nitrogen, and adding the
25 boron as a copper-boron master alloy at the last possible moment. The molten
mixture is then continuously cast into strip of width 50mm and of thickness 10
mm, after which an impurity-rich surface layer of at least 0.1 mm is scalped off
the surface of the cast strip by a metal planer. The cast strip is then cold rolled to
5mm thickness, annealed at 620-650°C for 30-45 minutes in a slightly wet
30 protective gas atmosphere containing 0.1-0.5% oxygen and having a dew point of
20-40°C, these conditions being selected to promote formation of GeO₂ without

oxidizing copper to copper oxides, then subjected to a second rolling to a thickness of 2.5 mm and a second annealing, after which the "as cast" grain structure has been substantially removed and the sheet can be formed by a silversmith without exhibiting objectionable orange-peel effects.

5 The rolled annealed sheet has a measured hardness of 64 HV which is comparable to values for Sterling silver. A sample of the rolled sheet can be annealed by heating to about 600°C followed by quenching, and the procedure can be repeated six times, after which the sample is in good condition apart from slight edge cracking and exhibits no fire-stain. This behaviour differs from that of
10 normal Sterling silver which tends to crack if quenched from red heat, and also from that of 925 Argentium whose low-melting (554°C) ternary silver-copper-germanium eutectic would be liquid at the quenching temperature and would cause the alloy to shatter when quenched.

15

Example 2

(Production and properties of investment cast strip)

The molten alloy of Example 1 is formed into strip by investment casting. The resulting strip is substantially free of "hot short" defects and brittleness, and
20 has a hardness of 63.5 HV.

Example 3

Solvent dip cleaning (solvent degreased samples)

25 Solutions are made up containing stearyl mercaptan (0.1, 0.5 and 1.0 gram) in EnSolv 765 (100 ml). Samples of the rolled annealed ternary alloy sheet of Example 1 which have been polished and ultrasonically degreased in EnSolv 765 for 2 minutes are each immersed in one of the stearyl mercaptan solutions for periods of 2 minutes, 5 minutes and 15 minutes. The samples are then buffed with
30 clean cotton wool.

- 20 -

In order to evaluate tarnish resistance, the alloy samples are supported on a glass slide in a fume cupboard about 25mm above the surface of 20% ammonium polysulphide solution so as to be exposed to the hydrogen sulphide that arises from that solution. All of the samples demonstrate good tarnish resistance during a one-hour test, with very slight yellowing after 45 minutes exposure to the hydrogen sulphide. The light film on the samples is easily removed with a cleaning cloth impregnated with stearyl mercaptan.

By way of comparison, a standard Sterling silver sample starts to discolour as soon as it is subjected to the above test and after one hour had forms a heavy black tarnish which can not be removed with a cleaning cloth impregnated with stearyl mercaptan.

Example 4

Effect of post-treatment solvent cleaning

Example 3 is repeated for the ternary alloy samples except that instead of buffing with cotton wool after the mercaptan treatment, the samples are ultrasonically degreased in EnSolv 765 for 2 minutes. The samples are then tarnish tested as described in Example 3 and all show enhanced tarnish resistance. The ability of the protective effect of the stearyl mercaptan treatment to survive ultrasonic cleaning in EnSolv suggests that the tarnish resistance is achieved by a surface reaction involving the stearyl mercaptan and possibly the germanium in the present alloy, and not by formation of a grease or oil layer on the surface of the present alloy.

Example 5

Aqueous dip application (solvent degreased samples)

An anti-tarnish treatment solution is prepared using the following ingredients:

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	Stearyl mercaptan	1g
	EnSolv 765	5 ml
	Detergent (Fairy Liquid)	40 ml
5	De-ionised water	100 ml

The Stearyl Mercaptan is dissolved into the EnSolv 765 after which the resulting solution is mixed with detergent (Fairy Liquid) and diluted with water to provide an aqueous dip. Samples of the ternary alloy of Example 1 are polished and ultrasonically degreased in EnSolv 765 for 2 minutes, immersed into the above aqueous dip for 2 minutes at ambient temperatures and then rinsed under running tap water. It may be noted the water is immediately repelled from the polished surface, which leaves the samples dry. Samples may be tarnish tested as described in Example 3 and all show enhanced tarnish resistance.

Example 6

Direct "Sponge" Application - Neat Detergent Solutions (solvent degreased/ aqueous degreased samples)

20

The following solutions are prepared:

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid) (Preferred quantities)
- 25 - 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml soap (liquid hand soap)

The stearyl mercaptan is initially dissolved into the EnSolv. The detergent is then mixed into the solutions. Samples of the rolled annealed alloy of Example 1 are polished and ultrasonically degreased in EnSolv 765 for 2 minutes. The stearyl mercaptan/EnSolv/detergent solutions are then directly applied to the

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surface of the samples using damp cotton wool and massaged into lather. The samples are then rinsed under running tap water. In each case, it is noted that water is repelled off of the polished surface, leaving the samples dry. Samples are tarnish tested as in Example 3 by being exposed to neat ammonium polysulphide solution over a period of 1 hour. They all show enhanced tarnish resistance. The above direct "sponging" method for applying the Stearyl Mercaptan is tested on ternary alloy strip samples degreased in a 2% Fairy Liquid aqueous solution. Enhanced tarnish resistance is again achieved.

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CLAIMS

1. A ternary alloy of silver, copper and germanium containing from more than 93.5 wt% to 95.5 wt% Ag, from 0.5 to 3 wt% Ge and the remainder, apart
5 from incidental ingredients (if any), impurities and grain refiner, copper.
2. The alloy of claim 1, wherein the weight ratio of Cu to Ge is from 4:1 to 3:1.
- 10 3. The alloy of claim 2, wherein the weight ratio of Cu to Ge is about 3.5:1.
4. The alloy of any preceding claim, containing from 1.0 to 1.5 wt% Ge.
5. The alloy of claim 4, containing about 94.5 wt% Ag, about 4.3 wt% Cu
15 and about 1.2 wt% Ge.
6. The alloy of any preceding claim, further comprising boron in an amount effective for grain refinement.
- 20 7. The alloy of any preceding claim, containing 1-40 ppm of boron.
8. The alloy of any preceding claim, containing 5-20 ppm of boron.
9. A finished or semi-finished shaped article of the alloy of any preceding
25 claim.
10. The article of claim 9, which is formed by casting.
11. The article of claim 9, which is at least partly produced from sheet or strip.

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12. Use of an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide for the surface treatment of an alloy according to any of claims 1-8.
13. The use of claim 12, wherein the alkanethiol, alkyl thioglycollate, dialkyl
5 sulfide or dialkyl disulfide has C₁₂-C₂₄ alkyl groups.
14. The use of claim 12 or 13, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in an organic solvent.
- 10 15. The use of claim 14, wherein the solvent containing the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is generally neutral.
16. The use of claim 14 or 15, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in a solvent based on n-propyl bromide.
15
17. The use of claim 12 or 13, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is in (a) a composition obtainable by dissolving said alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in an organic solvent and adding to said solution a relatively concentrated aqueous soap or detergent, or (b) an aqueous dispersion obtainable by dissolving said
20 alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide in an organic solvent, adding to said solution a relatively concentrated aqueous soap or detergent, and diluting the resulting mixture with water.
- 25 18. The use of claim 12 or 13, wherein the alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide is contained in a polish or impregnated into a polishing cloth.
19. The use of any of claims 12-18, wherein the alkanethiol or
30 alkylthioglycollate is selected from stearyl mercaptan, cetyl mercaptan (octadecyl mercaptan), stearyl thioglycollate and cetyl thioglycollate.

INTERNATIONAL SEARCH REPORT

national Application No

T/GB2004/002317

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	GB 2 255 348 A (METALEUROP RECH) 4 November 1992 (1992-11-04) cited in the application claim 2 page 3	1-5
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/002317

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB2004/002317

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